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STRUCTURAL FEATURES OF 2,4-DINITROIMIDAZOLE (24DNI)

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A single-crystal x-ray diffraction study verified that the target oxidizer molecule 2,4-dinitroimidazole (24DNI) was synthesized by thermal rearrangement of 1,4-dinitroimidazole. 24DNI crystallizes in the orthorhombic space group, Pbca, with unit-cell dimensions: a = 10.127(2), b = 18.497(2), c = 6.3337(2) Å. and Z = 8 and has a density of 1.770 g/cm^3. Positions of the heavy atoms were determined with direct methods and the hydrogen atoms were located with difference Fourier methods. The structure was refined to a final R value of 0.060 [493 reflections with $I > 3\sigma(I)$]. The molecular [N(1)-H(1). . .N(3)], hydrogen bonded in the a direction which are held together in the lateral directions by molecular forces. Some structural features of 24DNI are compared with those of 1,4-dinitroimidazole.

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CONTENTS

INTRODUCTION

Dinitroimidazole (DNI), C3H2N404, is an energetic aromatic molecule which may have potential as a high energy/density oxidizer for use in gun propellants (ref 1). However, this molecule can exist as several different isomers with respect to substituted nitro group positions. Since each isomer has different properties which can affect the practical utility of this molecule as a propellant oxidizer, characterization of each form is necessary before DNI can be used in a propellant formulation.

The 2,4-dinitroimidazole (24DNI) isomer which probably is more stable than 1,4-dinitroimidazole (14DNI) which contains a nitramine group, is now under consideration as a potential oxidizer substitute for cyclic nitramines currently used in solid gun propellant formulations. This structure study was done primarily to confirm the identity of the target isomer.

EXPERIMENTAL

This laboratory attempted to make 24DNI by thermal rearrangement of 14DNI (ref 2). The resulting powdery product was then recrystallized in acetonitrile to produce prismatic single crystals.

X-ray Data Collection

A pale yellow prismatic crystal of 24DNI synthesized at this laboratory, having approximate dimensions of 0.15 x 0.05 x 0.05 mm, was mounted on a glass fiber. The preliminary examination and data collection were performed with Cu Kα X-radiation. (λ = 1.54178 Å) on a Rigaku ASC5r computer controlled diffractometer equipped with a graphite crystal incident-beam monochromater and a 12 kW rotating anode generator.

The cell constants presented in table 1 and orientation matrix for data collection were obtained at 23 ± 1°C from least squares refinement using setting angles of 18 carefully centered reflections in the angular range of 40.82 deg < 2θ < 59.96 deg.

The intensity data also were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique [θ scan width of 1.78 + 0.14 tan θ)] at a scan rate of 8.0 deg/min (in omega) to maximum 2θ value of 120.0 deg. To assure good counting statistics, the intensities of weak reflections {I < 15σ (I)] were measured by accumulating the counts from four successive rescans. Stationary background counts were measured on each side of the reflection. The ratio of peak counting time to background was 2:1.

Intensities of three representative reflections measured after every 120 reflections remained constant throughout data collection. This indicated both electronic stability and that the crystal did not degrade during the course of data acquisition.

Data Reduction

Lorentz-polarization, absorption and secondary extinction corrections (table 1) were applied to the intensity data. The x-ray scattering factors were taken from Cromer and Waber (ref 3). Anomalous dispersion effects for heavy atoms were included in the structure factor calculations (ref 4) and the values of f' and f" were those of Cromer (ref 5). On the basis of systematic absences, space group Pbca was selected.

Structure Determination

Non-hydrogen atom positions were found by direct methods (ref 6) and the hydrogen atom positions were located by difference Fourier techniques. The hydrogen atom positions were refined isotropically while heavy atoms were refine anisotropically by full-matrix least squares. The function minimized was $\Sigma w (|Fo| - |Fo|)^2$ where w is defined as $4Fo^2/\sigma^2(Fo)^2$. The structure was refined to a final R value of 0.060 using 493 reflections [$I > 3\sigma (I)$] out of 1,075 measured reflections.

Pertinent crystallographic data, atomic coordinates, and equivalent temperature factors, bond lengths, and bond angles are presented in tables 1 through 4, respectively. Unit-cell packing diagrams viewed down the c axis and a axis are shown in figures 1 and 2, respectively. A molecule of 24 DNI with its atom numbering scheme is shown in figure 3.

RESULTS AND DISCUSSION

The title compound crystallizes in the orthorhombic space group Pbca with a = 10.127 (2), b = 18.487 (2), and c = 6.333 (2) Å. The atomic coordinates and equivalent temperature factors for the 24DNI asymmetric unit which contains three carbon atoms, two hydrogen atoms, four nitrogen atoms, and four oxygen atoms are given in table 2. The symmetry operations of this space group generate eight formula weights of 24DNI which results in a calculated x-ray density of 1.770 g/cm^3.

Description of the Crystal Structure

The molecular packing consists of infinite chains of adjacent 24DNI molecules hydrogen bonded by N(1) - H(1). . .N(3) in approximately the a direction (fig. 1). This H-bond approaches linearity with a bond angle of 170(6) deg and H(1). . .N(3) and N(1). . .N(3) having values of 1.81(7) and 2.829(7) Å, respectively. Alternate

molecules within the chain are coplanar while the adjacent molecules are inclined about 120 with each other. This wig-wag conformation is clearly shown in figure 2. Weaker molecular forces operate on the molecules in the lateral directions. The three shortest non-hydrogen bonded heavy atom contacts are 2.92(1) and 2.94(1) and 2.999(9) Å for 0(22)--0(22), 0(41)--C(4), and 0(41)--N(2), respectively.

Description of the 2,4-Dinitroimidazole Molecule

In figure 3, it is shown that the nitro groups are, indeed, substituted on C(2) and C(4) positions of the imidazole ring in the target molecule. The nitro groups substituted on C(2) and C(4) are designated 2-nitro and 4-nitro, respectively. The 24DNI molecule is not planar, but the imidazole moiety is planar with a mean displacement of 0.0045 Å from the least-squares plane. The C(2) ring atom has the largest displacement of 0.009(7) Å and C(4) has the smallest displacement of 0.001(7) Å.

The N(2) atom of the 2-nitro group is coplanar with the imidazole ring while the N(4) bond of the 4-nitro group is displaced -0.032 Å from the ring. The planes of the 2-nitro and 4-nitro groups are also twisted out of the imidazole plane by 0.7 deg and 7.9 deg, respectively.

In 14DNI (ref 7), the average displacement from the ring is 0.0014 Å, with C(4) having the largest displacement [0.002(2) Å] and N(1) the smallest [0.000(2) Å]. In contrast to 24DNI, both nitro-group nitrogen atoms, N(4) and N(11), are displaced from the ring on opposite sides of the plane by 0.019(2) Å and by -0.049(2) Å, respectively. The 1-nitro group and 4-nitro group are also twisted 9.4 deg and 1.9 deg out of the imidazole plane, respectively.

The interatomic distances in the 24DNI imidazole moiety (table 3) are intermediate between single and double bond lengths. This suggests that the ring bonds are partial double bonds. In general, the magnitudes of these bond lengths are typical of bonds found in aromatic heterocyles.

The shortest C-N bond is C(2)-N(3) [1.286(8) Å] which suggests a degree of double bond localization. This double bond localization may be characteristic of imidazole and its nitro derivatives since it has been observed as the shortest C-N bond in imidazole [1.316(2) Å (ref 8)], in 4-introimidazole [1.317(2) Å (ref 9)], in 2-nitroimidazole [1.318(3) Å (ref 10)], and in 14DNI [1.300(3) Å (ref 7)].

A comparison of the ring bonds with those of 14DNI, reveals that C(4)-C(5) [1.370(9) Å] in 24DNI is somewhat longer than its counterpart in 14DNI [1.354(3) Å] , but, conversely, all of its C-N bonds are shorter than its 14DNI counterparts.

As observed with 14DNI, the imidazole-ring bond angles at nitro-group sites (table 4) are significantly larger while the ring bond angles adjacent to the nitro groups are significantly smaller than observed in unsubstituted imidazole. This nitro-group effect on the imidazole ring which may be a result of nitro-group electron affinity is further illustrated by comparing 24DNI with 14DNI. In 24DNI, the ring bond-angles are C(2)-N(1)-C(5) [106.0(6) deg], N(1)-C(2)-N(3) [115.0(7) deg], and N(3)-C(4)-C(5) [115.0(7) deg], while in 14DNI the counterpart angles are 109.9 (2) deg, 110.3(2) deg, and 114.1(2) deg, respectively.

The bond lengths and bond angles observed in the nitro groups are in agreement with generally accepted values for these parameters.

An unexpected, but interesting aspect of this structure determination is the rather high standard deviations displayed in the bond lengths (±0.009). In other imidazole derivative structures, the reported bond length standard deviations are in the range of ±0.001 to ±0.003.

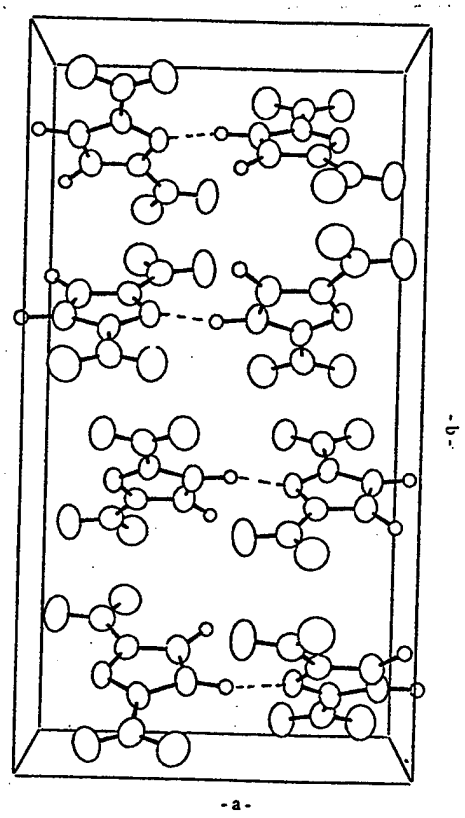
Initially, it was assumed that poor crystal quality might be responsible for the high standard deviations. Repeated recrystallization, however, neither improved the R value nor the bond-length standard deviations.

Another possible explanation for these high standard deviations is that there is disorder in the crystal resulting from incomplete nitro-group substitution on the four positions of the imidazole ring during thermal rearrangement. This could result in some mixed crystal or defect crystal formation. A structure determination of 24DNI synthesized by another method might resolve this question.

CONCLUSIONS

1. The 2,4-dinitroimidazole (24DNI) isomer was synthesized by thermal rearrangement of the 1,4-dinitroimidazole isomer.

2. The structure data also suggested the possibility of some disorder in 24DNI prepared by the thermal rearrangement method.



Hydrogen bonds depicted as dashed lines.

Figure 1
Unit cell of 2,4-dinitroimidazole (24DNI) (viewed down the c axis)

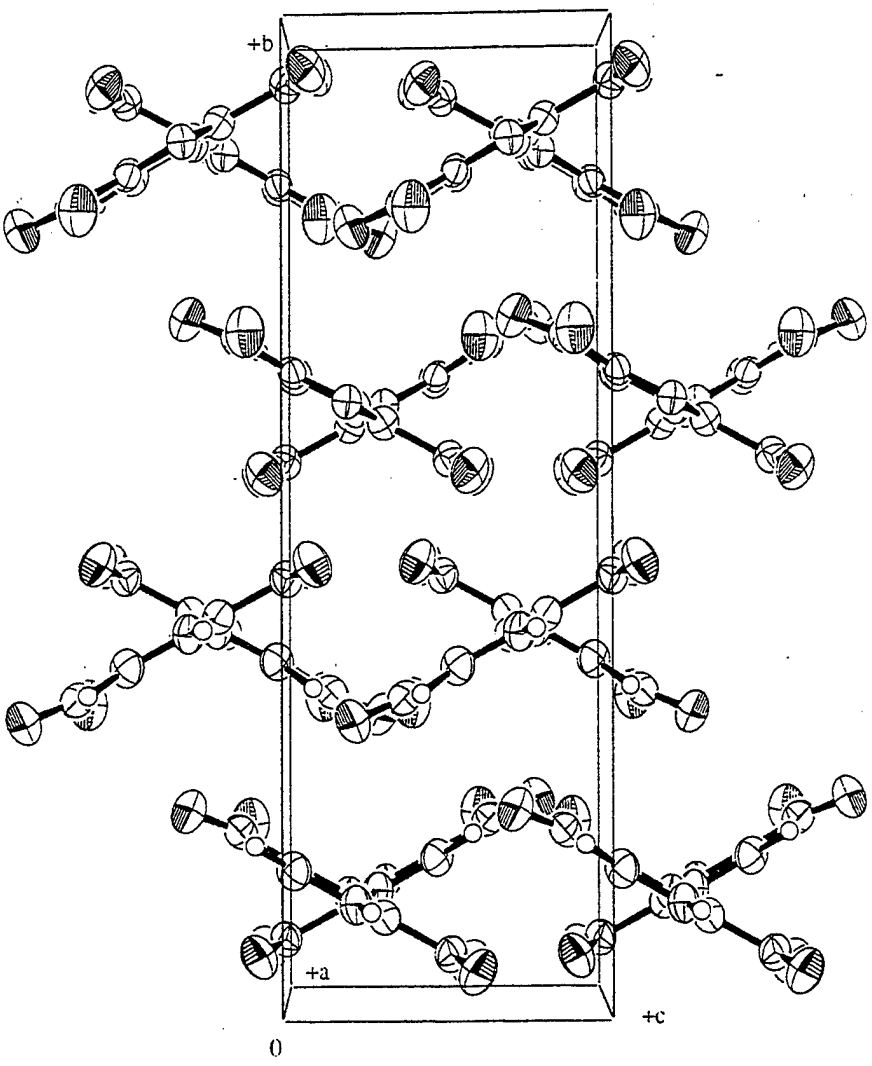


Figure 2
Unit cell of 2,4-dinitroimidazole (24DNI) (viewed down the a axis)

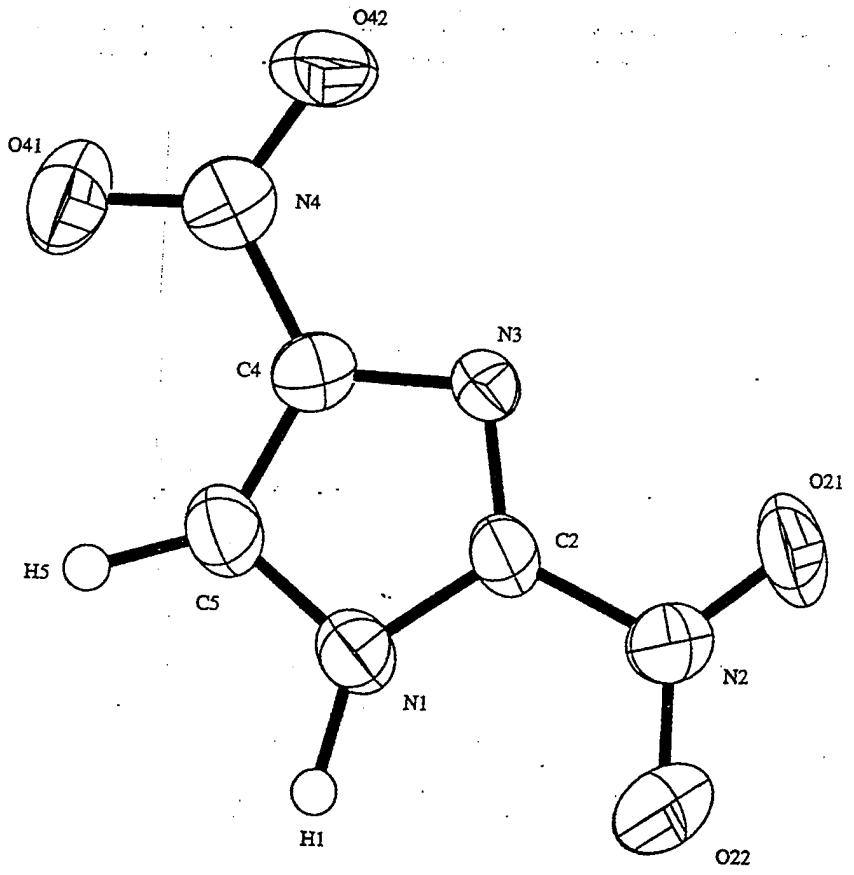


Figure 3
2,4-dinitroimidazole (24 DNI) molecule and atom numbering scheme

Table 1
24DNI crystal data colected at 23±1°C*

Molecular formula	C3H2N404
Formula weight	158.07
Crystal System	Orthorhombic
Space group	Pbca (#61)
a	10.127(2) Å
b	18.497(2) Å
c	6.333(2) °
V	1186.3(5) $Å^3$
Z	8
D	1.770 g/cm^3
λ (Cu K∝)	1.54178 Å
u	14.10 cm^{-1}
F(000)	640
Scan type	ω - 2θ
20 max	120.0
Total reflections	1075
No. reflections	493
[I > 3.σ (I)]	
h	0 to 11
k	0 to 20
	0 to 7
Secondary extinction	1.8528E-06
Absorption transmission factors	0.98 - 1.00
R; Rw	0.060; 0.066
GOF	2.89
Final Diff Fourier	
Max peak	0.31 e^-/A^3
Min peak	-0.25 e^-/A^3

*X-ray diffraction data collected by Molecular Structure Corp., The Woodlands, TX.

Table 2
Atomic coordinates and equivalent thermal parameters
and their esd's in parentheses for 24 DNI

Atom	x/a	y/b	z/c	Beq*
0(21)	0.3200(5)	0.0478(3)	0.5722(9)	5.1(3)
0(22)	0.1043(6)	0.0450(3)	0.5898(9)	5.4(2)
0(41)	0.2608(6)	0.2046(3)	-0.292(1)	5.3(3)
0(42)	0.4380(5)	0.1890(3)	-0.1087(9)	5.1(3)
N(1)	0.0813(5)	0.1139(3)	0.217(1)	3.5(3)
N(2)	0.2112(6)	0.0603(3)	0.507(1))	3.7(3)
N(3)	0.3013(5)	0.1189(3)	0.1948(9)	2.7(3)
N(4)	0.3175(6)	0.1825(3)	-0.137(1)	3.8(2)
C(2)	0.2010(7)	0.0976(4)	0.303(1)	3.0(2)
C(4)	0.2425(6)	0.1494(4)	0.028(1)	3.0(3)
C(5)	0.1072(7)	0.1478(4)	0.031(1)	3.7(4)
H(1)	-0.024(7)	0.110(3)	0.26(1)	5(2)
H(5)	0.032(6)	0.173(3)	-0.06(1)	3(1)

Table 3
24DNI bond lengths in angstroms (Å) and their esd's in parentheses

Atom	Atom	Distance	Atom	Atom	Distance
0(21)	N(2)	1.198(7)	N(2)	C(2)	1.471(9)
0(22)	N(2)	1.235(7)	N(3)	C(2)	1.286(8)
0(41)	N(4)	1.205(7)	N(3)	C(4)	1.338(9)
0(42)	N(4)	1.240(7)	N(4)	C(4)	1.432(9)
N(1)	C(2)	1.363(8)	C(4)	C(5)	1.370(9)
N(1)	C(5)	1.357(9)	C(5)	H(5)	1.08(8)
N(1)	H(1)	1.10(9)			

Table 4
24DNI bond angles in degrees and their esd's in parentheses

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(2)	N(1)	C(5)	106.0(6)	N(1)	C(2)	N(2)	121.2(7)
C(2)	N(1)	H(1)	139(4)	N(1)	C(2)	N(3)	115.0(7)
C(5)	N(1)	H(2)	115(4)	N(2)	C(2)	N(3)	123.8(7)
O(21)	N(2)	0(22)	128.1(7)	N(3)	C(4)	N(4)	121.5(6)
O(21)	N(2)	C(2)	117.2(6)	N(3)	C(4)	C(5)	115.0(7)
O(22)	N(2)	C(2)	114.7(6)	N(4)	C(4)	C(5)	123.5(8)
C(2)	N(3)	C(4)	101.4(6)	N(1)	C(5)	C(4)	102.6(7)
O(41)	N(4)	0(42)	123.7(7)	N(1)	C(5)	H(5)	123(3)
C(41)	N(4)	C(4)	119.1(7)	C(4)	C(5)	H(5)	134(3)
O(42)	N(4)	C(4)	117.1(7)				

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